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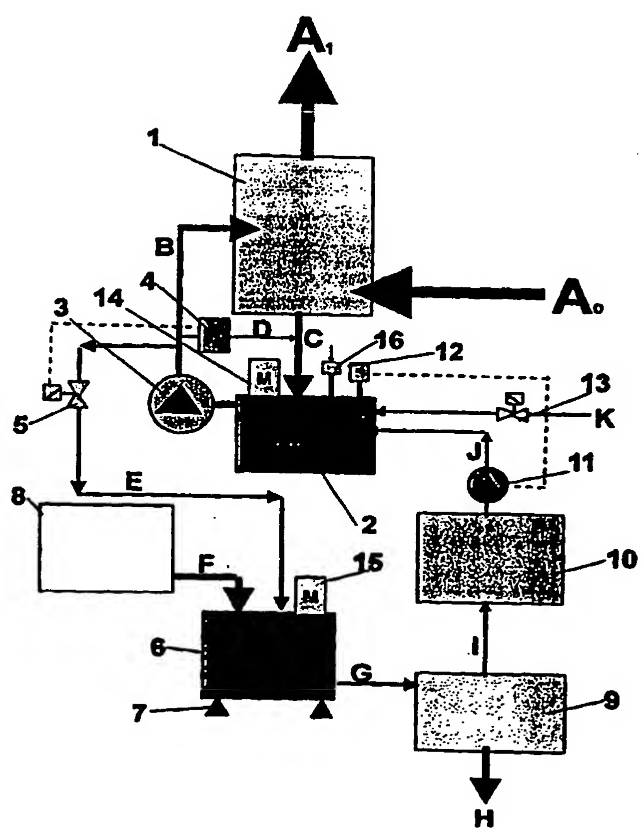
(54) Title: DESULFURISATION OF FLUE GASES BY DUAL ALKALISATION

(57) Abstract

The present invention relates to a method for recovering and treating of sulfur dioxide (SO_2) contained in flue gases. In the method, flue gases are passed as a stream (A_0) to a washer part (1). Circulated washing liquid is fed to the washer part (1) from a first container (2) through a flow line (B), and neutralized by alkali metal neutralization, whereby sulfur dioxide (SO_2) contained in flue gases dissolves in said circulated washing liquid. Said circulated washing liquid is oxidixed, whereby alkali sulfate is formed in the first container (2). In the method, the alkali sulfate concentration of the circulated washing liquid in the first container (2) is measured, and, the concentration of the circulated washing liquid having reached a predetermined value, said liquid is passed from said first container (2) as a stream (E) into a second container (6), wherein the circulated washing liquid is at least partially ion exchanged with a base containing calcium (Ca), whereby gypsum ($CaSO_4$), and alkali hydroxide are formed in the second container (6).



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Desulfurisation of flue gases by dual alkalisation

The present invention relates to a method for recovering and treating of sulfur dioxide contained in flue gases, wherein

a) flue gases are passed as a stream to a washer part

b) circulated washing liquid is fed to the washer part from a first container through flow line, and neutralized by alkali metal neutralization, whereby sulfur dioxide contained in flue gases dissolves in this circulated washing liquid

c) the circulated washing liquid is oxidized, whereby alkali sulfate is formed in the first container.

Stripping of sulfur dioxide from gases by washing is conducted in several ways. This washing process is a so-called wet washing wherein gas containing sulfur dioxide is contacted as intimately as possible with a washing liquid. As a result, the gas cools down and leaves the washing process at its dew point. The solubility of sulfur dioxide in the washing liquid essentially depends on several characteristics thereof, the most important of which being, however, its pH value and sulfur dioxide content. If the pH value is high, it is clear that no solubilized sulfur dioxide, but only sulfite salts will form. On the other hand, if the amount of washing liquid is great relative to the sulfur dioxide content of the gas, and if the saturation limit of solubility is far from being reached, it is evident that stripping of sulfur dioxide from gas by washing will be succesful.

There are several neutralizing agents. In small neutralizing plants with simple automation either alkali metal (Na and K) carbonates or hydroxides are used as

neutralizing agents. With these agents no harmful crystallization takes place in any parts or steps of the process. Moreover, the degree of neutralization will be high, generally over 90 %. A serious disadvantage is, however, the price of this neutralizing agent, making the neutralization more expensive, even by factor 10, compared to lime based neutralization used in large-scale plants. Therefore, alkali metal based neutralization is used only where complete sulfur dioxide removal is desired, as well as in small plants where the contribution of automation is significant. Wash water that is formed in washing by alkali neutralization contains sodium/potassium sulfite that will easily be oxidized to sulfates. This oxidation may be carried out by oxidizing directly the circulated wash water, or in a separate oxidizing reactor. Oxidation is not very sensitive to pH value, and also the ease thereof speaks for alkali neutralization.

Another and economically interesting neutralization method is to use lime either as carbonate, or lime-milk made from burnt lime, containing both dissolved and non-dissolved calcium hydroxide. In practice, this washing process is difficult to run. Moreover, it must be carried out very carefully, since calcium forms poorly soluble sulfurous acid when calcium sulfite is neutralized at pH value of 6 or above. This may easily lead to rapid formation of undesirable crystalline precipitates in the piping, pumps, or other parts of the washing process, often resulting in clogging, and even total interruption of the washing process. In the presence of calcium, the pH of the sulfur dioxide washing process should be below 6, even below 5.5. Calcium will then be present as a solubilized compound, as so-called calcium bisulfite [$Ca(HSO_3)_2$]. Calcium salt dissolved in this form will oxidize easily and produce calcium sulfate, or gypsum.

As already mentioned, as pH raises above 5.5, calcium causes harmful crystallization. For this reason the wash water cycle should be kept calcium free. To this end, several means and methods have been developed and found.

One of these is a so-called dual alkaline earth mixture, wherein not only calcium (Ca) but also magnesium (Mg) is used as a neutralizing agent. Magnesium salts such

as magnesium sulfate and sulfite are significantly more soluble than respective calcium salts. In this way, crystallizations clogging the process may often be eliminated, and the process is not so sensitive to the pH value as the process described above.

In dual alkalization the washing process is first neutralized with sodium or potassium hydroxide or carbonate. Thereafter the washing liquid is oxidized to form sulfate. The sulfates formed are preferably treated with calcium hydroxide to form again alkali hydroxides, whereby calcium is converted to gypsum. However, the solubility of gypsum is so high that special measures and treatments are necessary to avoid said crystallization of calcium. Accordingly, calcium ions are removed from the liquid as completely as possible, or it is attempted to get below the solubility limit of calcium sulfate, this solubility being 50 times lower that that of gypsum. An example of such chemical additions in calcium ion exchange is to add for instance sodium carbonate. Thereby the calcium ion content falls below said calcium sulfite solubility limit. This method is complicated, and must be carried out very precisely.

Other chemical additions are also used to eliminate calcium ions by precipitating them, or by forming thereof a complex soluble compound for the prevention of crystallization. Such acids as acetic acid, oxalic acid, tartaric acid, and others may be addded. Only few of them are in wider commercial use. The most common method is to use a lime ($CaCO_3$) based wash water cycle wherein the pH value remains below 5.5 Such a wash water cycle comprises a separate oxidation reactor step to form gypsum. Gypsum is removed from this wash water cycle, then washed and generally used in building industry to produce prefabricated elements. Such plants to wash sulfur dioxide are generally very large, and their automatic control is precise. They produce great amounts of waste water that are difficult to treat. Accordingly, also for this reason said wet washing plant requires high investment costs, and as a consequence, they are often too expensive for medium-sized companies. For this reason, there is a need to find other economical and useful solutions.

An object of the present invention is to provide a method to carry out the neutralizing washing of flue gases containing sulfur dioxide by dual alkalization, without producing waste water, wherein 70—95 % of this alkali metal, preferably for instance sodium (Na), may be recovered, thus avoiding the calcium ion risk, or harmful crystallisation.

The method according to the present invention is characterized in that

d) alkali sulfate concentration of the circulated washing liquid in the first container is measured, and

e) after the concentration of the circulated washing liquid has reached a predetermined value, the liquid is passed from the first container as a stream into a second container, wherein said circulated washing liquid is at least partially ion exchanged with a base containing calcium (Ca), whereby gypsum ($CaSO_4$), and alkali hydroxide are formed in the second container.

The method to treat the washing liquid according to the invention essentially simplifies the dual alkalization process used for the washing of gases containing sulfur dioxide. As a result, the automation, and especially the control of the acidity become easier, and the operation thereof is simplified. Essential in this invention is that no waste water is produced. The treatment of waste water is extremely expensive, considering not only the investment costs needed, but also especially the treatment thereof to the purity required by law. Not to mention that the automatic control of the purity thereof is a continuous process requiring active participation of the authorities. Even for investors it is essential that waste water is treated according to the standard requirements.

Two main significant objects are achieved with the present invention. Accordingly, the waste water problem is eliminated, and the expensive neutralizing agent is recovered and recycled. The saving in the use of alkali metals is at least 70-80%.

This saving is very significant not only considering the expenses, but also for the nature.

A preferable embodiment of the method is based on controlling/measuring the specific weight of the wash water to adjust the desired sodium sulfate concentration as desired, whereby a measured amount of liquid with a known concentration is taken from the wash water cycle, and is substoichiometrically treated using burnt lime or calcium hydroxide with a known concentration, using most preferably about 0.5—0.9 times the amount of sodium sulfate (the relation of calcium to sulfur, Ca:S, being 0.5—0.9). Thus a gypsum precipitate forms in the liquid, the solubility of calcium therefrom being negligible owing to the substoichiometric treatment, since the liquid contains sodium sulfate. The gypsum is filtered from the liquid, the precipitate may be washed, and then the alkali hydroxide solution is returned to neutralization where it is evaporated with the humidity of the gas at its dew point, thus avoiding waste waters.

The invention is now described in more detail with reference to a preferable embodiment of the method of the present invention shown in the figures of the appended drawings, without wishing to limit the invention solely thereto.

Figure 1 is a schematic side view of a preferable embodiment of the equipment used in the method of the present invention.

Figure 2 is a schematic side view of a preferable embodiment of the specific weight measurement used in the method of the present invention.

Referring now to Figure 1, a gas stream A_0 containing sulfur dioxide SO_2 flows to a washer 1, to which a pump 3 feeds a wash water stream B. This wash water is taken by the pump 3 from a container 2 for circulated water that receives from the washer 1 after the washing step the used wash water stream C containing the impurities present in the gas stream A_0. A side stream D of the stream B leaving the pump 3 is passed through a device 4 for measuring the specific weight/concentration.

An embodiment of this device 4 for measuring the specific weight is shown in figure 2, and explained in connection thereto. It measures, coincident with the stream B, the specific weight of the side stream D, both streams B and D having the same composition. In this determination, mainly the change of the specific weight due to different Na_2SO_4 concentration is measured, this change being directly proportional to the concentration of sodium sulfate. This correlation between Na_2SO_4 concentration and specific weight may be verified with a few separate samples.

The device 4 for measuring the specific weight of the circulated water, corresponding to its Na_2SO_4 concentration, from the side stream D, delivers data to a valve 5, preferably a magnetic valve. Preferably, this valve directs part of the stream B leaving the pump 3 as an ion exchange stream E into a reactor 6, the liquid volume or weight therein being controlled with volume measurements, or respectively using for instance a weighing technique 7, known as such. When a metered/desired amount of Na_2SO_4 solution/washing liquid, the concentration of which is known while determined by the device 4 for measuring the specific weight in the container for circulated water, is passed into the reactor 6, a calculated amount of powdery/liquid $CaO/Ca(OH)_2$ with a known concentration is fed as a calcium stream F from a $CaO/Ca(OH)_2$ container 8 to carry out the ion exchange Na 6 Ca in the degree desired. Substoichiometrically calculated, the calcium content of the stream F should be (Ca:S = < 1), preferably 10% below the stoichiometric value of 1.

In the reactor 6, the Na_2SO_4 containing liquid of the ion exchange stream E reacts with calcium ions contained in the calcium stream F, whereby sodium Na replaces the calcium ion to produce sodium hydroxide (NaOH). Sulfate and calcium ions form gypsum ($CaSO_4$) that precipitates in the form of a hydrated compound ($CaSO_4$ + $2H_2O$). Sodium hydroxide is dissolved in the wash water. Due to this ion exchange reaction the pH value in the reactor 6 rises even to 14.. Ion exchange may be made more effective for instance with a mixer 15. After a suitable mixing and ion exchange reaction period the reactor 6 is drained as a stream G via sedimentation/filtration step 9. Gypsum and any solid matter present in the washing liquid leave this step as a stream H, and as dry as possible, and the filtrate is removed as a stream I into the

container 10 for neutralizing agent. In the sedimentation/filtration step 9, the stream H may be washed with fresh water/liquid, which is preferably combined with the stream I.

In the container 2 for circulated water the device 12 for measuring the pH value, and so the acidity, controls the metering pump 11 of the container 10 for neutralizing agent to neutralize (stream J) the sulfur dioxide dissolved in the washer I of the washing process from the gas stream A_0 in the washing liquid stream C. This dissolved sulfur dioxide forms sulfurous acid that is then oxidized with an oxidizing agent 14, preferably in the container 2 for circulated water.

Since the humidity of the gas stream A_0 to be washed is generally low, the dew point thereof being between 20 and 30° C, its water content is low. The gas stream A_1 leaves the washer 1 at its dew point, and at least at the temperature of 50°C. The water content thereof is at least 3 times higher than before the washer 1. Accordingly, water is continuously removed from the wash water cycle. This removed water is partly made up by stream J, but the most part is compensated by a fresh water/liquid stream K, regulated by a liquid level 16 controller, and passing through a valve, preferably a magnetic valve, 13, preferably into the container for circulated water 2.

Figure 2 shows an exemplary, but in no way limitative device for measuring specific weight for easy determination of the Na_2SO_4 concentration in the washing liquid, this device being an essential part of a preferable embodiment of the present invention. This device 20 comprises a balance 21, with a pipe coil thereon 22 comprising a pipe loop with desired length and diameter. The loop contains a predetermined amount of flowing liquid, the volume thereof being for instance one liter. In practice, a stream D is taken through valve 23, in this case through for instance a magnetic valve, from the stream B passing to the washer 1. The stream D flows through the pipe coil 22 for weighing the total weight thereof by balance 21 that preferably feeds the data to a central control unit 30. Thereafter, for comparison, liquids/media b and c with known specific weights may be separately passed through valves 24 and 25, whereby the central control unit 30 determines the specific weight of the stream D on the basis

of these weights. If now for instance two specific weights relative to Na_2SO_4 concentration are also measured from the stream D, then the Na_2SO_4 content in the liquid passing to ion exchange may be measured very precisely based on the amount thereof. Without wishing to limit the invention in any way, however, the operation and object of the invention may easily be carried out with this method for measuring the amount of sodium sulfate passing to the treatment.

The removal of calcium ions from the water of the stream I, or the solubility of gypsum is prevented by the chemical reaction and solubility equilibrium constants. In chemistry, these reactions and solubilities may be represented by equations as follows:

1) Gypsum dissolves in water to form ions: $CaSO_4 \rightarrow Ca^{++}- + SO_4^{--}$

2) Equilibrium constant = $$Kp = \frac{CCa \times CSO_4}{CCaSO_4} = \text{constant}$$

If a solution contains only gypsum, it dissolves as shown in the equation. In practice, the solubility of gypsum is about 400 mg of calcium/liter.

If the solution also contains sodium sulfate Na_2SO_4, the solubility thereof at 50°C is at least 350 g/liter of washing liquid, that is, more than 80-fold in comparison to that of gypsum. If now according to the invention for instance 10% of the sodium sulfate is left in free form, that is, is not ion exchanged with calcium ions, the amount of SO_4 radicals in the solution becomes so high that the concentration of gypsum is significantly higher than that based on the solubility constant, or mathematically, about 87.5 times higher. As a result, in the Kp equation $CCa \times CSO_4$, the CCa concentration becomes negligible. Accordingly, the concentration of calcium dissolving from gypsum is significantly below 1 mg/l. This prevents the formation of $CaSO_3$ common in washing processes, since the concentration of calcium dissolving there-

from is higher that the said solubility of gypsum, if it already contains 10% Na_2SO_4 solution.

The method according to the present invention may of course be applied to other ion exchange processes, if necessary. The only disturbing factor in the application of the present invention is any solid dust present in the gas stream A_0 that may interfere with the determination of specific weight, if the proportion thereof is significant. For this reason, it is advisable to analyse the specific weight curve with not only the media b and c, but also with two different compositions of the stream D, to get a more precise sodium sulfate concentration in the stream D.

The batch treatment embodiment disclosed in the description is not a prerequisite, since ion exchange may be carried out continuously using controlled/regulated streams E and F with known concentrations and flow rates, taking the desired stoichiometry into account. Then, the mixing container 6, and its mixer 15 comprise no measuring devices.

Claims

1. Method for recovering and treating of sulfur dioxide (SO_2) contained in flue gases, wherein

a) flue gases are passed as a stream (A_0) to a washer part (1),

b) circulated washing liquid is fed to the washer part (1) from a first container (2) through a flow line (B), and neutralized by alkali metal neutralization, whereby sulfur dioxide (SO_2) contained in flue gases dissolves in said circulated washing liquid,

c) said circulated washing liquid is oxidized, whereby alkali sulfate is formed in the first container (2),

characterized in that

d) alkali sulfate concentration of the circulated washing liquid in the first container (2) is measured, and

e) the concentration of the circulated washing liquid having reached a predetermined value, said liquid is led from said first container (2) as a stream (E) into a second container (6), wherein the circulated washing liquid is at least partially ion exchanged with a base containing calcium (Ca), whereby gypsum ($CaSO_4$), and alkali hydroxide are formed in the second container (6).

2. Method according to claim 1, **characterized** in that the alkali sulfate concentration of said circulated liquid in the first container is determined by measuring the specific weight thereof.

3. Method according to claim 1 or 2, **characterized** in that said alkali hydroxide is recycled as a stream (G,I) from the second container to a third container (10) as neutralizing agent.

4. Method according to claim 3, **characterized** in that said second container is drained as a stream (G) to a sedimenting/filtering container (9) wherefrom gypsum ($CaSO_4$), and any solid matter contained in said washing liquid are removed as a stream (H), and the filtered alkali hydroxide is passed as a stream (I) to the third container (10).

5. Method according to any claim 1—4, **characterized** in that alkali hydroxide is passed from said third container (10) to said first container (2) as a stream (J).

6. Method according to any claim 1—5, **characterized** in that make-up washing liquid is fed as a stream (K) to said first container.

7. Method according to any claim 1—6, **characterized** in that the acidity of said circulated washing liquid in the first container (2) is measured with a device (12) for measuring pH value.

8. Method according to any claim 1—7, **characterized** in that the amount of said circulated washing liquid passed to the second container (6) is determined by weighing with a balance (7), and that powder/liquid containing calcium (Ca) is fed as predetermined a stream (F) to the second container (6) from a container (8).

9. Method according to any claim 1—8, **characterized** in that the amount of said circulated washing liquid in the first container is controlled with a liquid level controller (16).

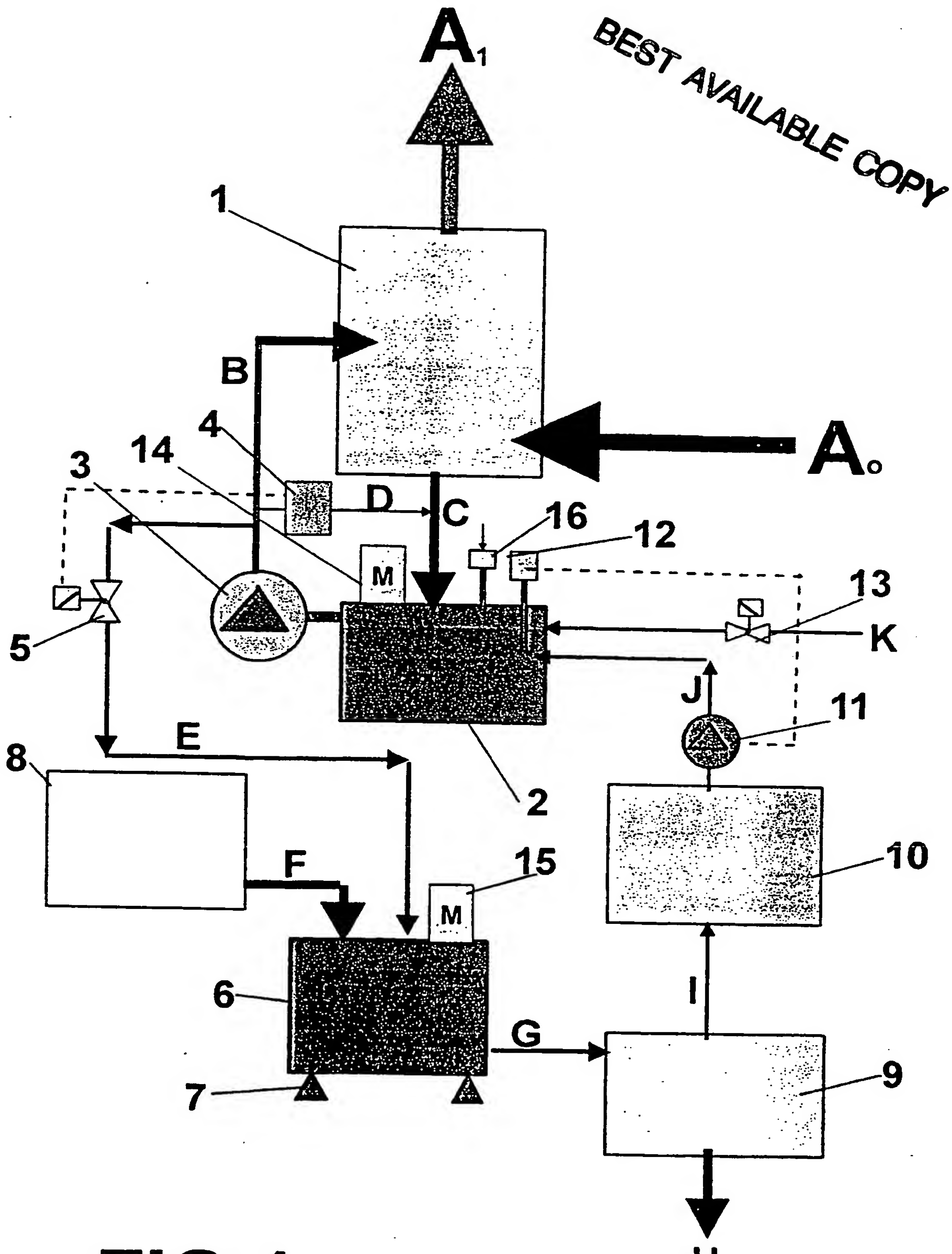

FIG 1

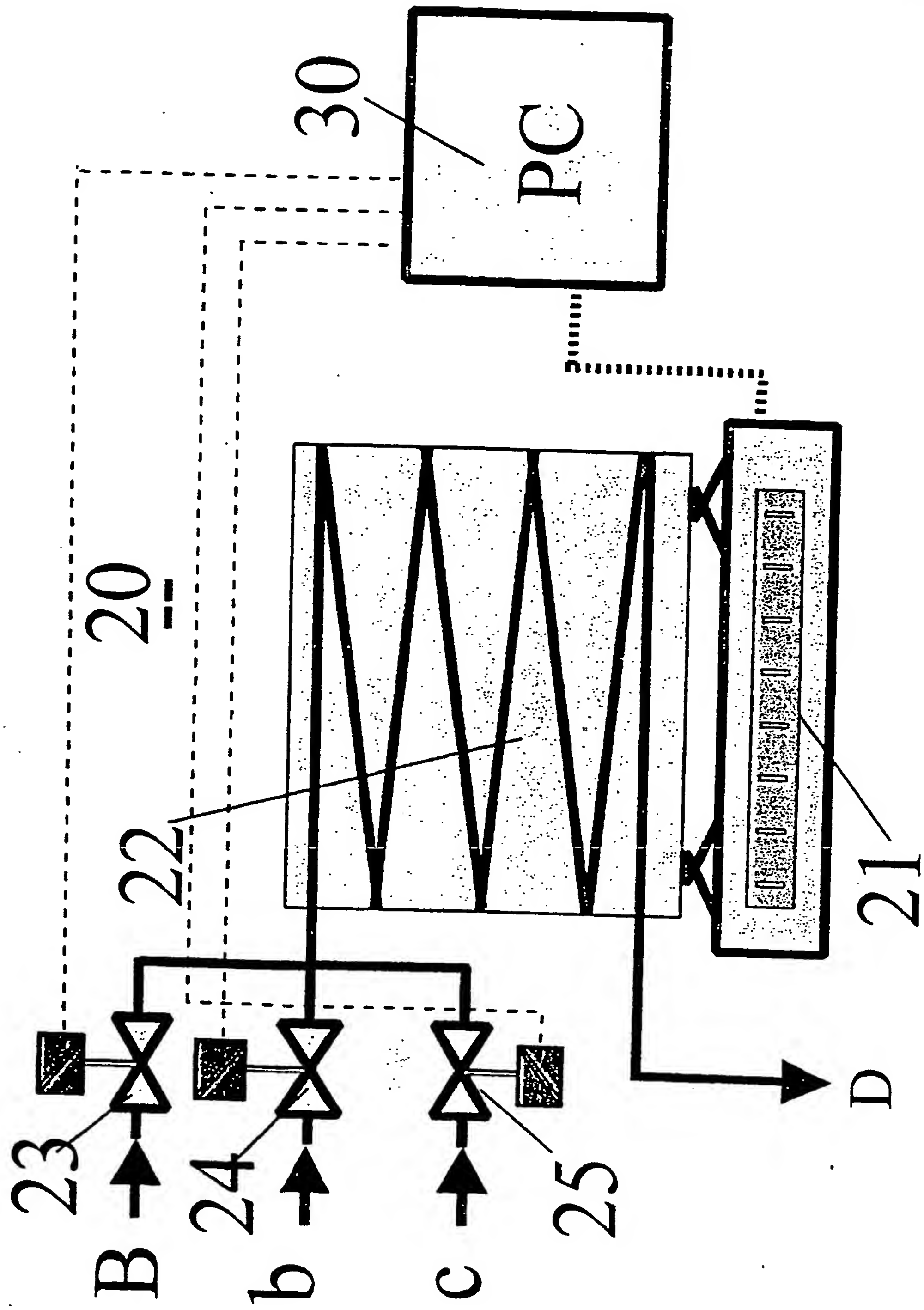

FIG 2

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B01D 53/50
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 99/00371

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

02/08/99

International application No.
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